Initiation Mechanisms in Radical Polymerization: Reaction of Isopropoxyl Radicals with Methyl Methacrylate

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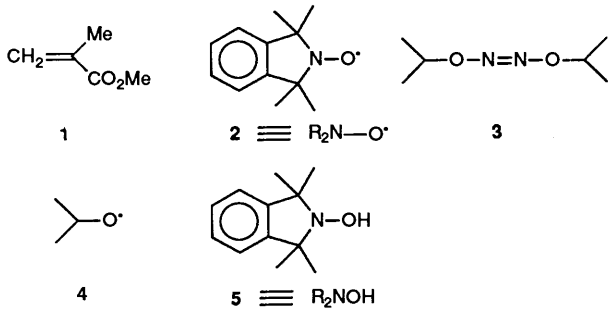
The radical trapping technique employing 1,1,3,3-tetramethyl-1,3-dihydroisoindole-2-yloxyl **2** as a scavenger has been used to study the reaction of isopropoxyl radicals with methyl methacrylate **1**. Addition to the unsubstituted (tail) end of **1** and hydrogen abstraction from the α-methyl group of **1** were the major pathways of the reaction; the ratio of addition–abstraction was 7:1. The formation of alkoxy amines **6** and **8** was an unusual feature of the reaction. These two products appear to be derived from the reaction between 2-hydroxy-1,1,3,3-tetramethyl-1,3-dihydroisoindole and **1**. The mechanism of this reaction is discussed.

The work described in this paper is part of an ongoing investigation into the effect of alkoxyl radical structure on the mechanism of the reaction of alkoxyl radicals with commercially important vinyl and acrylic monomers. In general, alkoxyl radicals participate in many reactions and can undergo either intermolecular or intramolecular reactions (such as hydrogen abstraction, double bond addition and β-scission). Previous studies have covered the reaction of a wide range of monomers with t-butoxyl radicals,[1] cumyloxyl radicals,[2] as well as hydroxyl radicals;[3] this work examines the reaction of a secondary alkoxyl radical, the isopropoxyl radicals **4**, with methyl methacrylate **1**. The reaction of ethoxyl radicals with **1** and of both radicals with styrene and with other selected monomers will be described in future papers. The radical trapping technique has been described previously.[4]



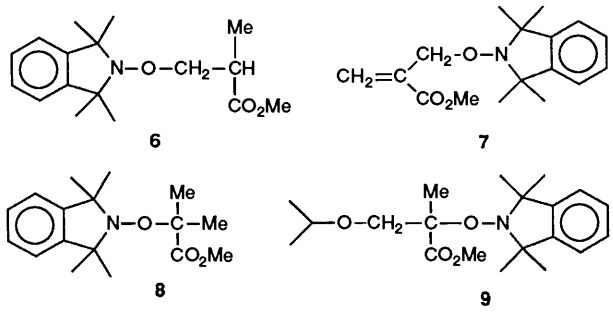
Isopropoxyl radicals **4** were generated by the thermal decomposition of diisopropyl hyponitrite **3**.[5] Although the general family of hyponitrites has undergone extensive scrutiny as a potential source of initiators,[6–8] **3** has not been specifically mentioned; in fact we have no reference indicating that **4** (derived from **3**) has ever been investigated as a polymerization initiator. This is the first report of a study of the mechanism of the reaction of isopropoxyl radicals **4** with monomers in solution.

Results and Discussion

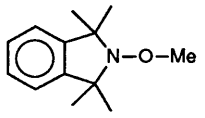
Following the reaction of initiator **3** (0.020 mol dm^{-3}) with methyl methacrylate **1** in the presence of trap **2** (0.044 mol dm^{-3}) in neat monomer at 60 °C *in vacuo* for 10 h (9 half lives), the products **6–9** were isolated by HPLC and characterized by NMR. Relative yields are given in Table 1. The major product **9** and minor product **7** arise by the expected, traditional routes of radical attack on monomer followed by trapping as depicted in Scheme 1. Products from head addition and abstraction from the ester methyl by isopropoxyl radicals were not detected showing that these processes are relatively unimportant (<0.5%) in this system. (Abstraction of H-atoms from the ester methyl was observed in the corresponding reaction of **1** with *tert*-butoxyl radicals.[1a]) Similarly, the absence of 2-methoxy-1,1,3,3-tetramethyl-1,3-dihydroisoindole **10** (formed by the coupling of a methyl radical with the nitroxide **2**) among the reaction products shows that the rate of β-scission of the isopropoxyl radical **4** is relatively much slower than that of the *tert*-butoxyl radical under similar reaction conditions (**10** was observed in the corresponding reaction of **1** with *tert*-butoxyl radicals in the presence of **2**[1a]). This is

Table 1 Relative yields of alkoxy amines **6–9** from the reaction of **1** and **3** in the presence of 2.2 mol. equiv. of **2** at 60 °C

		Yield (%)			
Entry	Reaction time(h)	**6**	**7**	**8**	**9**
1	0.5	<0.5	12.0	3.5	84.0
2	1	<0.5	12.0	3.5	84.0
3	2	1.6	12.6	5.9	79.9
4	3	2.9	12.3	8.0	76.8
5	5	3.9	12.7	10.6	72.9
6	10	6.0	13.0	12.9	68.0
7	96	32.6	4.7	49.7	12.7



consistent with the results of Walling *et al.*[9] who found that the amount of β-scission relative to H-abstraction from cyclohexane, decreased by about 100-fold from tertiary alkoxyl radicals to primary alkoxyl radicals.



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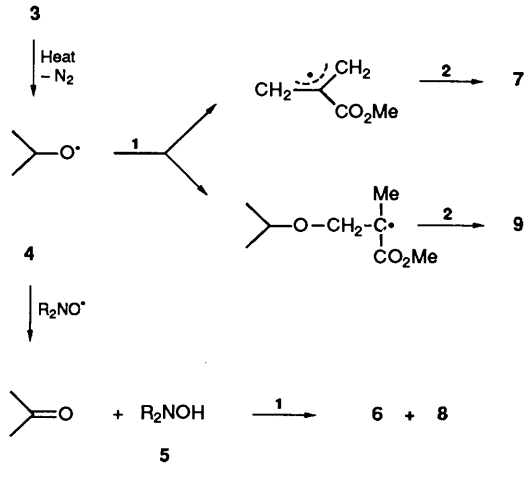
From Table 1, it can be seen that the ratio of **9**–**7** (addition–abstraction) decreases slowly with time (from an initial value of 7:1 to 5.2:1 after 10 h, when most of the initiator **3** has been consumed). This is presumably due to a slow decomposition of **9** under the reaction conditions.[10] The ratio of addition to abstraction has therefore been taken as 7:1, the initial value observed over the first hour of the reaction. This value is significantly greater than the corresponding ratios for the reaction of **1** with *tert*-butoxyl radicals[1a] (2.3:1) or with cumyloxyl radicals[2] (2.5:1), suggesting that steric factors in the radical hinder the addition process in the case of the latter two.

The appearance of products **6** and **8** shows that reactions other than isopropoxyl radical attack on monomer occur in this system. The influence of reaction time (see Table 1), and the concentration of nitroxide trap (see Table 2), on the relative product yields, indicates that the nitroxide **2** takes part in a slow side reaction to produce **6** and **8**. One possibility is that the labile hydrogen atom on the isopropoxyl radical **4**, or on its precursor **3**, is abstracted by **2** to form acetone and **5**, which then reacts with monomer **1** to form **6** and **8** (see Scheme 1). A possible route by



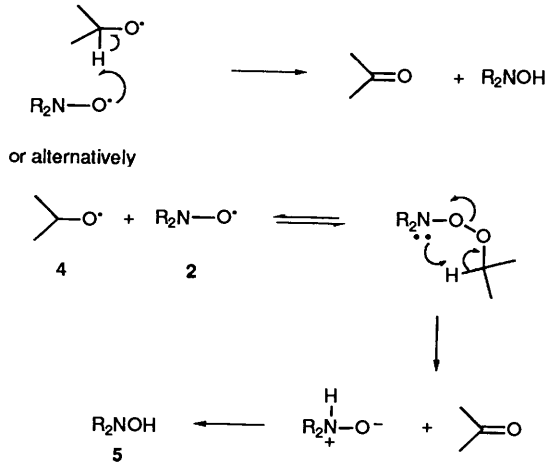
Scheme 1

which **4** and **2** may react to form acetone and **5** is shown in Scheme 2. Hydrogen abstraction from the initiator **3** by **2** seems unlikely as the rate of decomposition of **3** was not accelerated by the presence of **2** [the $t_{\frac{1}{2}}$ of a 2 × 10^{-3} mol dm^{-3} solution of **3** in isooctane at 60 °C was measured (by HPLC, UV detection at 230 nm) as 71 min. When **2** (2.2 equiv.) was also present, the $t_{\frac{1}{2}}$ was measured as 77 min, indicating, if anything, a small inhibition of decomposition (by removing isopropoxyl radicals, induced decomposition is removed)].[11] If **4** is reacting with **2** to form acetone and **5**, then effectively there will be competition between the monomer **1** and the nitroxide **2** for the isopropoxyl radicals. This should mean that as the concentration of **2** is increased, relatively less **9** (and **7**) should be formed. This was found to be the case (Table 2). Moreover, it was found that when the volume of monomer **1** was increased by a factor of four (*i.e.* nitroxide and initiator concentration reduced four-fold) the absolute amount

Table 2 Relative yields of alkoxy amines **6**–**9** from the reaction of **1** (solvent) with **3** (0.020 mol dm^{-3}) in the presence of various concentrations of nitroxide **2** at 60 °C

	Products (%)			
Concentration of **2** (mol dm^{-3})	**6**	**7**	**8**	**9**
0.022[a]	0.7	14.3	3.0	82.0
0.044[b]	3.9	12.7	10.6	72.9
0.080[b]	9.1	10.5	20.1	60.3
0.120[b]	13.8	8.5	24.0	53.7

[a] Reaction time: 70 min (one half life of initiator). [b] Reaction time: 5 h.



Scheme 2

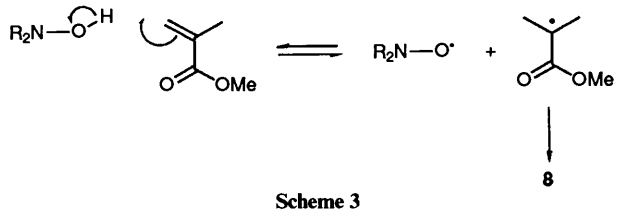
of **9** doubled (against an internal standard; both reactions 1 h at 60 °C), thus lending strong support for a (competitive) reaction between the nitroxide **2** and isopropoxyl radicals.

The presence of **5** in the reaction mixture was confirmed by HPLC (after 5 h at 60 °C, the amount of **5** was approximately ten times the amount of **9** present). The presence of acetone and of isopropyl alcohol was confirmed by GLC (abstraction of hydrogen from **1** by isopropoxyl radicals would give isopropyl alcohol and **7**).

In a separate experiment we have shown that **5** reacts slowly (less than 10% reaction after 5 h at 60 °C) with monomer **1** to produce **6** and **8** in the ratio of 1:2.7 which is similar to the ratio observed in the main experiments. It is clear that as the reaction time is increased, this slow reaction between the methacrylate and **5** will become more important. Thus, after 96 h, **6** and **8** had become the major products of the reaction (Table 1).

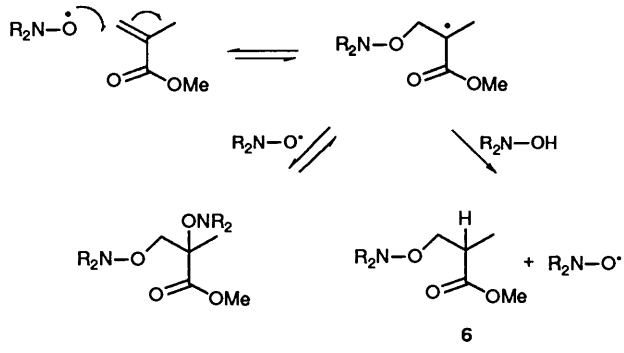
The reaction between **5** and methyl methacrylate to give **6** and **8** is intriguing. Although **6** is formally the product of Michael addition and is not unexpected,[12] the major product **8** is the result of addition in the opposite sense. We believe that the formation of **8** may be an example of a molecule-assisted homolysis (MAH)[13] reaction, involving transfer of a hydrogen atom to the acrylate (Scheme 3). An analogous reaction between **5** and styrene has been reported[14] while the thermal polymerization of styrene probably also takes place *via* a MAH mechanism.[15] It can also be seen from Table 1 that the ratio of **6**–**8** increases with time (from about 1:3 after 3 h to 2:3 after 96 h). This presumably reflects the relative stability of **6** and **8** under the reaction conditions (either reversible formation of **8** or its slow decomposition would account for this change in ratio—very hindered systems such as **8** are rather unstable and tend to revert to their precursor radicals[10]).

What is more puzzling is that the ratio of **6**–**8** also increases with increasing nitroxide concentration (Table 2). A possible explanation for this effect is that the formation of **6** occurs not



Scheme 3

via a 'normal' Michael addition mechanism, but *via* a radical-catalysed Michael as outlined in Scheme 4. Increasing the concentration of nitroxide catalyst would clearly increase the rate of formation of **6**.



Scheme 4

Conclusions

Although the nitroxide trap causes complications by partaking in a disproportionation reaction with the initiating isopropoxyl radicals to produce **5**, **6** and **8**, this process simply reduces the number of isopropoxyl radicals available for reaction with the monomer. It does not alter, to any significant extent, the ratio of addition to abstraction processes occurring between isopropoxyl radicals and monomer. The use of low concentrations of nitroxide and short reaction times (say one half life or less) minimizes these side reactions.

This investigation has shown that isopropoxyl radicals add tail-wise to methyl methacrylate at seven times the rate they abstract from the α-methyl group of the monomer, and that hydrogen abstraction from the ester methyl is not observed. The results show that isopropoxyl radicals are much more selective for tail addition than either *tert*-butoxyl or cumyloxyl radicals in their reaction with methyl methacrylate. This indicates that if isopropoxyl radicals were used to initiate the polymerization of methyl methacrylate, the proportion of initiator-derived unsaturated end groups should be much lower than if *tert*-butoxyl or cumyloxyl radicals were used.

Experimental

General Methods.—Melting points were determined on a Buchi 'Tottoli' silicone-oil bath melting-point apparatus, and are uncorrected. NMR spectra were recorded on a Bruker CXP-300 spectrometer, with deuteriated chloroform as solvent and tetramethylsilane as internal standard. All *J* values are in Hz. HPLC was performed using either a Du Pont instrument 850 liquid chromatograph fitted with an Altex Ultrasphere ODS column, connected to a Du Pont UV spectrophotometer set at 270 nm and a LDC 308 computing integrator, or using a Varian 5000 liquid chromatograph fitted with an Altex Ultrasphere ODS column, connected to a Vari-chrom detector also set at 270 nm. Microanalyses were performed by the Australian Microanalytical Service AMDEL, Melbourne.

Materials.—Methyl methacrylate **1** was purified by washing with 5% NaCl, dried over anhydrous sodium sulphate, and distilled at reduced pressure prior to use. Diisopropyl hyponitrite[5] **3** was prepared from isopropyl bromide and silver hyponitrite with or without solvent (pentane or diethyl ether) at 0 °C; the hyponitrite (22% yield) obtained can be purified by crystallization in MeOH at −78 °C, and it could be stored in a freezer (−20 °C) for weeks without significant decomposition. The first order rate constant for thermal decomposition of **3** in isooctane solution (4×10^{-3} mol dm^{-3}) was found to be 1.6×10^{-4} s^{-1} at 60 °C ($t_{\frac{1}{2}}$ 71 min). This compares favourably with a recent literature value *k* 1.36×10^{-4} s^{-1} at 60.1 °C.[10] 1,1,3,3-Tetramethyl-1,3-dihydroisoindolin-2-yloxyl **2** was prepared by the literature procedure.[16]

2-Hydroxy-1,1,3,3-tetramethyl-1,3-dihydroisoindoline **5** was prepared in quantitative yield by the hydrogenation of nitroxide **2** with Adam's catalyst (PtO_2) at atmospheric pressure using dichloromethane as solvent.[17] 2-Cyclohexyloxy-1,1,3,3-tetramethyl-1,3-dihydroisoindoline was obtained according to the literature procedure[18] and was used as an internal standard for the HPLC analyses.

General Procedure for the Reaction of Methyl Methacrylate with Diisopropyl Hyponitrite in the Presence of Nitroxide **2**.—A solution of diisopropyl hyponitrite **3** (1 mmol), 1,1,3,3-tetramethyl-1,3-dihydroisoindolin-2-yloxyl **2** (1.1–6 mol equiv.) and freshly distilled methyl methacrylate (50 cm^3) was degassed by three successive freeze-pump-thaw cycles to 10^{-2} Torr, the reaction vessel was then sealed under vacuum. The reaction mixture was then heated at 60 °C for either 0.5 h or 1–10 h, and subsequently analysed by reverse-phase HPLC. The conditions used for HPLC analysis were: flow-rate, 2.5 cm^3 min^{-1}; solvent, 82% methanol in water for 25 min, then linear programmed to 100% methanol over the following 15 min, and finally maintained at 100% methanol. Excess of monomer was removed by distillation under reduced pressure prior to reverse-phase HPLC. New compounds (alkoxyamines **6**–**9**) were isolated (in order of elution from the HPLC column) and characterized by the spectroscopic and other data listed below.

Methyl 2-Methyl-3-(1,1,3,3-tetramethyl-1,3-dihydroisoindolin-2-yloxy)propanoate **6**.—(Found: MH$^+$, 291.393. $C_{17}H_{25}NO_3$ requires *M*H 291.394); δ_C 14.2 (q, *Me*CH), 25.0, 29.9 (br s, ring methyls), 39.7 (d, Me*C*H), 51.6 (q, OMe), 67.4 (s, C-1, C-3), 78.8 (t, OCH_2), 121.4 (d, C-4, C-7), 127.2 (d, C-5, C-6), 145.2 (s, C-3a, C-7a) and 175.5 (s, C=O); δ_H 1.25 (d, 3 H, ^3J 7.1, *Me*CH), 1.41 (br s, 12 H, 4 × *Me*), 2.82 (ddq, 1 H, ^3J 5.5, 7.1, 7.2, MeC*H*), 3.74 (s, 3 H, OMe), 3.99 (dd, 1 H, ^2J 8.8, ^3J 5.5, OCH_2), 4.10 (dd, 1 H, ^2J 8.8, ^3J 7.2, OCH_2), 7.08 (m, 2 H, 4-H, 7-H) and 7.21 (m, 2 H, 5-H, 6-H).

Methyl 2-[(1,1,3,3-Tetramethyl-1,3-dihydroisoindolin-2-yloxy)methyl]propenoate **7**.—This was identical to an authentic sample **1a** with the same retention time by HPLC; δ_C(249 K) 25.0, 29.9 (ring methyls), 52.1 (OMe), 67.1 (C-1, C-3), 75.7 (CH_2ON), 121.7 (C-4, C-7), 127.4 (C-5, C-6), 128.2 (CH_2=C), 136.6 (CH_2=*C*), 145.0 (C-3a, C-7a) and 166.8 (C=O); δ_H(330 K) 1.44 (s, 12 H, 4 × Me), 4.78 (s, 3 H, OMe), 4.66 (m, 2 H, CH_2ON), 5.93 (m, 1 H, CH_2=C), 6.32 (m, 1 H, CH_2=C), 7.07 (m, 2 H, 4-H, 7-H) and 7.20 (m, 2 H, 5-H, 6-H).

Methyl 2-Methyl-2-(1,1,3,3-tetramethyl-1,3-dihydroisoindolinyloxy)propanoate **8**.—M.p. 41–42 °C (Found: C, 70.4; H, 9.1; N, 4.6. $C_{17}H_{25}NO_3$ requires C, 70.1; H, 8.7; N, 4.8%); δ_C 24.9, 25.2, 29.6 (6 × Me), 51.8 (OMe), 67.8 (C-1, C-3), 81.2 (Me_2CON), 121.5 (C-4, C-7), 127.2 (C-5, C-6), 145.0 (C-3a, C-7a) and 175.5 (C=O); δ_H 1.38 (s, 6 H), 1.40 (s, 6 H), 1.53 (s, 6 H) (6 × Me), 3.74 (s, 3 H, OMe), 7.03 (m, 2 H, 4-H, 7-H), 7.18 (m, 2 H, 5-H, 6-H).

Methyl 3-Isopropoxy-2-methyl-2-(1,1,3,3-tetramethyl-1,3-di-

hydroisoindolin-2-yloxy)propanoate **9**.—M.p. 93–94 °C (colourless needles from pentane) (Found: C, 68.6; H, 8.7; N, 3.9. $C_{20}H_{31}NO_4$ requires C, 68.7; H, 8.9; N, 4.0%); δ_C 18.8 (q, *Me*–CON), 22.0 (q, Me_2CH), 25.3 (q), 25.5 (q), 29.6 (q, ring methyls), 51.7 (q, OMe), 68.0 (s, 68.1, C-1, C-3), 72.5 (d, Me_2CH), 73.2 (t, OCH_2), 84.1 (s, MeCON), 121.6 (d, C-4, C-7), 127.2 (d, C-5, C-6), 145.0 (s), 145.2 (s, C-3a, C-7a) and 173.8 (s, C=O); δ_H 1.13 (d, 3 H) and 1.16 (d, 3 H, ^3J 6.1, Me_2CH), 1.35 (s, 3 H), 1.36 (s, 3 H), 1.39 (s, 3 H), 1.47 (s, 3 H), 1.58 (s, 3 H, 5 × Me), 3.56 (d, 1 H, ^2J 9.0, OCH_2CON), 3.60 (heptet, 1 H, ^3J 6.1, Me_2CH), 3.71 (d, 1 H, ^2J 9.0, OCH_2CON), 3.77 (s, 3 H, OMe), 7.08 (m, 2 H, 4-H, 7-H) and 7.22 (m, 2 H, 5-H, 6-H).

Acknowledgements

One of us (S. H. T.) wishes to thank Griffith University for a Postgraduate Research Award and the C.S.I.R.O. for financial support. This work was also supported by the A.R.C.

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Paper 1/00429H
Received 29*th January* 1991
Accepted 12*th February* 1991